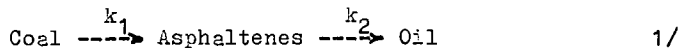


ASPHALTENES AND PREASPHALTENES - COMPONENTS OF AN ORIGINAL hvb COAL

Anna Marzec, Teresa Krzyżanowska, Danuta Bodzek

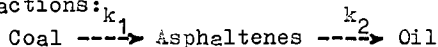
Petroleum and Coal Chemistry Dpt., Polish Academy of Sciences
44-100 Gliwice, 1-go Maja 62 St., Poland

Asphaltenes are considered to be the principle intermediates in the conversion of coal to an oil products. Weller /1/ stated that the catalytic conversion of coal involves two consecutive first order reactions:



At 400°C k_1 was reported as 27 times higher than k_2 and at 440°C k_1 as 10 times higher than k_2 .

Liebenberg and Potgieter /2/ derived another mechanism which includes the following reactions:



He tentatively determined the sum k_1+k_2 at 400°C and 440°C in the conversion of coal with tetralin and no catalyst added.

More recently Yoshida et al. /3/ established that the mechanism for catalytic conversion of Hokkaido coals includes Reaction 1 and 3. It is worth to emphasize that according to their experiments k_4 is considerably higher or lower than k_1 and k_2 , depending upon coal type.

Sternberg et al. /4,5/ have proposed that preasphaltenes are the intermediates between coal and asphaltenes. Contrary to this, Schwager and Yen /6/ considered that "preasphaltenes may arise from reactive coal depolymerization moieties, which are ... repolymerized into materials more difficult to degrade than the original coal substance".

Collins et al. /7/ claim that "carbon-carbon scission must be considered as an important factor in asphaltene formation" and in preasphaltenes formation as well. The statement has arisen from their experiments based on thermal treatment /over 300°C/ of model compounds - arylalkanes, diphenylalkanes and aryl alkyl ethers.

We have found that asphaltenes and preasphaltenes are the components of coal extracts. Coals were extracted at ambient temperature and precautions in analytical procedure have been observed. Therefore, the components of the extract may be considered they are the components of original coal.

EXPERIMENTAL

High volatile A bituminous coal J /vitrinite 60%, inertinite 33%, exinite 6%/ and hvab coal W /vitrinite 45%, inertinite 45%, exinite 10%/ have been investigated. Proximate and ultimate analyses are presented /Table 1/.

EXTRACTION

Coal samples / <1,4mm/ were extracted in the Soxhlets at ambient temperature for 150 hours. Benzene-ethanol 7:3 vv mixture has been applied. Yields and ultimate analysis of the extracts are given /Table 1/. Although the yields are low they are considerably higher than benzen extract or ethanol extract yields.

Temperature curriculum of the extracted compounds: after extraction at ambient temperature the extract solution has been influenced by temperature below 100°C /the bottom flask of the Soxhlet water bath heated/ for 18 hours /after each 18-hour period, solution has been removed and fresh solvents poured/. The total extract solution was carefully filtrated and the solvents were evaporated from it in a rotary apparatus at 50°C and reduced pressure.

FRACTIONATION OF THE EXTRACTS

has been carried out according to the scheme /Fig. 1/ based on the procedure described by Schweighardt et al./8, 9/ for analysis of hydrogenated coal liquids.

The following group components have been isolated /Table 2/:
preasphaltenes i.e., benzene insolubles/pyridine solubles
asphaltenes i.e., benzene solubles/hexane insolubles
basic fraction of asphaltenes
acidic/neutral fraction of asphaltenes
benzene and hexane solubles

Temperature curriculum of the extracted compounds, continued: all group components were freed from the solvents in a rotary apparatus at 50°C /except pyridine insolubles/ and reduced pressure to constant weight /except pyridine solubles/. Other analytical works were done at ambient temperature. Samples were stored in nitrogen.

Extract+benzene /10g:100ml/ were vigorously stirred for 3 hours. Benzene insolubles BI were filtrated, washed, dried, weighed. Then pyridine was added to BI and total - stirred for 1 hour. Pyridine insolubles PI were filtrated, washed and dried above 100°C to constant weight.

The content of pyridine solubles PS has been determined by difference:

BI - PI = preasphaltenes,
since some final amount of pyridine cannot be removed from them at 50°C.

Solubility of preasphaltenes

We tried to redissolve the preasphaltenes in the same solvent mixture as applied in coal extraction /benzene:ethanol 7:3/. It has been stated that preasphaltenes isolated from the coal extract are easily dissolved at ambient temperature in the mixture, although they are insoluble in benzene or ethanol. Therefore, no indication of their polymerization /6/ which could contribute to a formation of preasphaltenes has been found.

Further analytical work on the separation of preasphaltenes by HCl saturation of benzene/ethanol solution has not been completed yet.

The benzene soluble portion of the extract is reduced in volume by nitrogen flush at 50°C until an approximate ratio 1g:5ml solubles: benzene is reached. Then BS concentrate is slowly introduced by drops into vigorously stirred hexane. Filtrated, washed and dried precipitate yields the content of asphaltenes.

The asphaltenes are dissolved in toluene, filtrated, then dry HCl is bubbled through the solution until no further precipitation is observed. Chloride precipitate is freed from HCl by toluene/1n aqueous NaOH treatment and after evaporation of toluene the content of basic portion of asphaltenes is determined. Compounds which did not form HCl adducts and remained in toluene were recovered by evaporation /nonbasic portion of asphaltenes/.

TLC ANALYSIS OF THE EXTRACT AND ITS SEPARATION PRODUCTS

Table 3. Thin-Layer Chromatography conditions

	Solvent system			Solvent ratio			Development cycle
	M	C	B	M	C	B	
extract	methanol	chloroform	--	1 : 1	-	-	1/2; full
preasph.	methanol	chloroform	benzene	1 : 1	: 1	-	full
bases	methanol	chloroform	--	1 : 1	-	-	full
nonbases	methanol	chloroform	--	1 : 1	-	-	1/2; full

Neutral gel /type MN-Kieselgel HF/ on 20x20 cm plates was used. Full development cycle was 16 cm high; 1/2 cycle is realized as follows; the plate is kept in the chamber until solvent reached 1/2 height, removed from chamber, dried under nitrogen, reinserted in chamber.

The applied spray reagents for functional group detection on TLC plates are presented /Table 4/.

Table 4. Thin-Layer Spray Reagents

Reagent	Functional group indication				Detection limit / g/
	Ar-OH Phenol type	N-H ring Pyrrol type	=N-ring Pyridine type	Ar-NH ₂ Amines	
Fast Blue Salt B	red- violet	brown- violet	--	yellow- orange	0,01
FeCl ₃ 3% in 0,5n HCl	violet	dark green	--	blue	0,01
Wachmeister's Reagent	yellow- violet	purple- brown	--	brown- green	0,1
Erlich's Reagent	--	violet ^a	light yellow	light yellow	0,05
Dragendorff's Reagent	--	--	orange	pink- red	0,1
Iodoplatinate	--	--	brown	beige	0,5

^a/after few hours

Preparation of the reagents is based on E. Merck handbook - "Anfärbereagenzien für Dünnschicht- und Papier-Chromatographie", Darmstadt, 1970. The same reagents were applied by us /10/ in analysis of hydrogenated coal liquids.

Results of TLC analysis of the coal extract as well as its separation products are summarized /Table 5/.

Table 5. Results of Spray Reagent Test:

	Ar-OH Phenol type	N-H ring Pyrrol type	Functional Group =N- ring Pyridine type	Ar-NH ^a Amine ²
Extract	+	+	+	+
Preasphaltenes	+	+	+	+
Asphaltene bases	---	---	+	+
Asphaltene acidic/neutral	+	+	---	---

a/ TLC-Spray Reagent indication of amine presence is not an irrefutable proof.

b/ Meaningless test - preasphaltenes are contaminated by pyridine during separation procedure.

The results indicate that asphaltenes derived from the coal extract contain heterocompounds which may be separated into basic and acidic/neutral fractions. Phenol and pyrrol derivatives are present in the acidic fraction, pyridine derivatives -- in the basic portion. We did not find any amphoteric substances in the basic nor in the acidic fraction. Therefore, the analogous results have been obtained in analysis of asphaltenes extracted from coal at ambient temperature /this paper/ and asphaltenes derived from the high temperature coal conversion products /5, 8, 9, 10/.

INFRA-RED SPECTROMETRY OF THE EXTRACT AND SOME SEPARATION PRODUCTS

Spectra have been recorded by C. Zeiss spectrophotometer Specord 71 IR Model /NaCl prism/.

Spectra of the extract in KBr pellet /curve A/, basic fraction /curve B/ and acidic/neutral fraction of asphaltenes /curve C/ - both in 2% CS₂ solutions, 0,6 mm fixed path length cell, are presented /Fig. 2/. CS₂ bands have been compensated by application of variable path cell² in reference beam.

Broad and high band in 3590-3050 cm⁻¹ range is a strong indication of the presence of hydrogen bonded heterocompounds in the extract.

Spectrum of bases shows:

in 3570-3100 cm⁻¹ range - weak, broad band which may arise from stretching vibrations of N-H group, free or/and hydrogen bonded; taking into account TLC-spray reagent test results /pyrrol type N-H and phenol type O-H excluded/ the above band arise from amine type N-H bond.

1730 cm^{-1} band indicates carbonyl group of cyclic unsaturated ketones, and/or diketones, and/or quinones. However, this band is absent in the extract spectrum. Therefore, oxidation of the basic fraction may be a reason.

Spectrum of acidic/neutral fraction shows:

in 3585-3550 cm^{-1} range - sharp band characteristic of free phenol O-H and/or intramolecular phenol O-H..... π orbital band;

in 3495-3100 cm^{-1} range - broad band characteristic of intermolecular O-H bonded group; absorption of pyrrol type N-H stretching and/or NH...OH vibrations occurs within the range as well;

sharp 1030 cm^{-1} band may arise from symmetric stretching vibrations of C-O-C aryl ethers and/or skeletal vibrations of furanes; the presence of furanes is indicated as well by 880 and 860 cm^{-1} dublet.

However, the assignment of all other bands has been carried out, it is not presented here, since complex composition of the samples limits its diagnostic value. On the other hand, part of it is clearly visible and trivial, for instance - higher content of aromatic and alkyl groups in acidic fraction than in basic fraction.

CONCLUSIONS

Asphaltenes and preasphaltenes are the components of an original coal. Therefore, some portions of these group components in coal liquefaction products are not the products of thermal nor catalytic conversion.

The real content of asphaltenes and preasphaltenes in an original coal is still an unanswered question. We have yet to know more on electron-donor and -acceptor properties of solvent mixtures as well as about strength of donor-acceptor bonds occurring in coal substance, if one intends to select solvent mixture capable of extracting total amount of these components from coal.

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TABLE 1. Proximate and ultimate analyses of the coals^{a/}
yields and ultimate analysis of the extracts

	Mad	Ash ^{ad}	V ^{daf}	C	H	N	S	O ^{b/}	Yield ^{c/}
Coal J	4,34	4,02	39,05	82,34	5,40	1,64	0,57	10,05	-
Extract from "	-	-	-	82,43	7,45	1,00	0,64	8,48	4,51
Coal W	4,90	9,00	37,40	80,67	5,11	1,40	0,87	11,95	-
Extract from "	-	-	-	82,65	7,08	1,15	1,55	7,57	4,47

a/ Ultimate analysis is given in wt % of daf coal

b/ By difference

c/ Yields of extract are given in wt % of daf coal

TABLE 2. Group composition of coal extracts

Group Composition	Content of the components in /wt %/ :				
	Extract from Coal J	Coal J ^{a/}	Extract from Coal W	Coal W ^{a/}	
Pyridine insolubles /PI/	1,1	0,04	1,0	0,04	
Treaspthaltenes /PS/	45,3	2,04	42,7	1,91	
Asphaltenes /HI/	23,4	1,06	27,5	1,23	
Bases	4,8	0,22	6,7	0,30	
Acids + neutral cpds	18,6	0,84	20,8	0,93	
Hexane solubles /HS/	22,5	1,02	24,2	1,08	
Lost	7,7	0,35	4,6	0,21	
TOTAL	100,0	4,51	100,0	4,47	

a/ Data are given in weight percent of daf coal

FIG. 4.

EXTRACT FRACTIONATION SCHEME

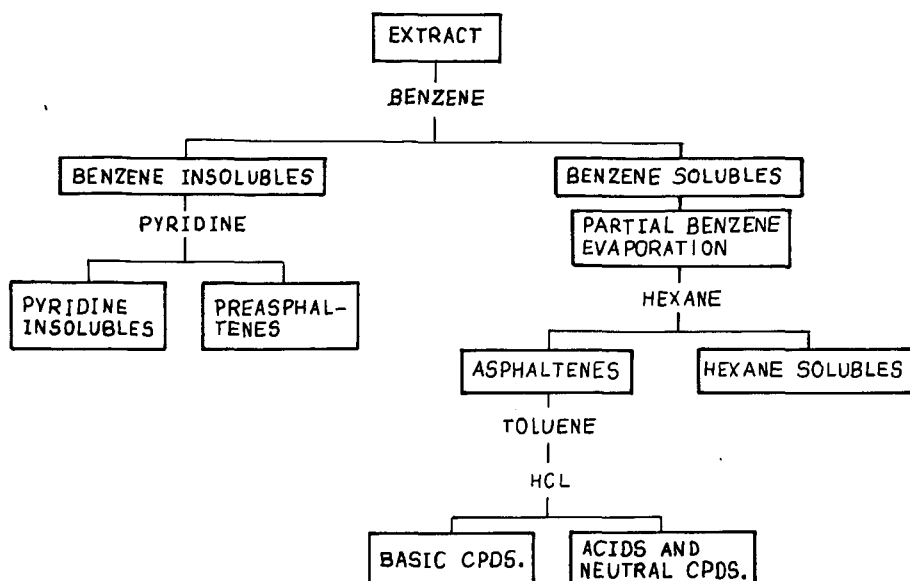


Fig.2 Infra - Red - Spectra of Analysed Products.

